Oxidation of Ammonia Nitrogen with Ozone in Water: A Mini Review

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Abstract
Since ammonia nitrogen is a pollutant causing eutrophication, it must be removed from wastewater to develop a sustainable environment and society. Ozonation, which is an oxidation reaction with ozone, is an effective and efficient method for the removal of ammonia nitrogen in wastewater because the reaction can proceed at low temperature and atmospheric pressure. Although the researches in ozonation of ammonia nitrogen have been going on for the last five decades, the reaction mechanism has not yet been well understood, and the papers focusing on the reaction mechanism are very few. In this short review paper, the progress in the oxidation of ammonia nitrogen with ozone both in non-catalytic and catalytic reactions is summarized to provide a better understanding of the reaction mechanism for ozonation of ammonia nitrogen in the water.

This mini review paper shows the progress in oxidation of ammonia nitrogen with ozone both in uncatalyzed and catalyzed reactions, since the reaction mechanism has not yet been adequately understood despite the research in this matter has been going on for the last five decades.

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Keywords: Ammonia nitrogen, Catalytic ozonation, Ozonation, Wastewater treatment

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Outline

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>18</td>
</tr>
<tr>
<td>Non-catalytic Ozonation of Ammonia Nitrogen</td>
<td>19</td>
</tr>
<tr>
<td>Homogeneous Catalysis for Ozonation of Ammonia Nitrogen</td>
<td>19</td>
</tr>
<tr>
<td>Br⁻ as a homogeneous catalyst</td>
<td>19</td>
</tr>
<tr>
<td>Cl⁻ as a homogeneous catalyst</td>
<td>21</td>
</tr>
<tr>
<td>Ozonation of ammonia nitrogen catalyzed with Pd²⁺ in the presence of Cl⁻: a preliminary report</td>
<td>22</td>
</tr>
<tr>
<td>Heterogeneous Catalysis for Ozonation of Ammonia Nitrogen</td>
<td>23</td>
</tr>
<tr>
<td>Heterogeneous catalysis over Co₃O₄</td>
<td>23</td>
</tr>
<tr>
<td>Heterogeneous catalysis over MgO</td>
<td>24</td>
</tr>
<tr>
<td>Heterogeneous catalysis over Pd/CeO₂</td>
<td>25</td>
</tr>
<tr>
<td>Conclusions</td>
<td>25</td>
</tr>
<tr>
<td>References</td>
<td>25</td>
</tr>
</tbody>
</table>

Introduction

Ammonia nitrogen is a nitrogen-containing compound that in wastewater mainly comes from excessive use of fertilizer, livestock excreta, and municipal sewage. In general, ammonia nitrogen exists as NH₄⁺ or NH₃ depending on pH of water ([NH₄⁺][OH⁻]/[NH₃], Kᵇ = 10⁻⁴.8) [1,2] and the ratio of NH₃ to NH₄⁺ in water increases with the increase of pH and temperature [3]. Although in nature, ammonia nitrogen is an important nutrient for the growth of the plants, excess concentration of it in water causes a serious threat to aquatic life and the environment. For instance, ammonia nitrogen is one of the major causes of the uncontrollable growth of algae in water (so-called eutrophication) that depletes the concentration of dissolved oxygen which further leads to the death of aquatic life [2]. Because
an increase in the concentration of ammonia nitrogen in surface water has recently been accelerated by rapid urbanization and industrialization [4], it is crucial to remove, ideally decompose, ammonia nitrogen from the water to develop sustainable environment.

Among the established technologies, ozonation, which is one of the advanced oxidation processes (AOPs) and oxidative decomposition of pollutants with ozone, is the most promising one for the removal of ammonia nitrogen from wastewater. This is because the reaction can proceed at low temperatures and atmospheric pressure and thus lowering energy demand, making this process even more applicable for industrial-scale applications.

Although the first paper on ozonation of ammonia nitrogen in wastewater was published almost five decades ago by Singer and Zilli [5], unfortunately, the understanding of the reaction mechanism is still poor. In fact, the papers published in this matter so far, before this review are very few. Why so? This motivated us to come out with this short review in purpose to summarize the research progresses on the ozonation of ammonia nitrogen. In addition to the summary of the previous investigations on the reaction mechanism both non-catalytic and catalytic reactions, this short review also provides some of our unpublished findings that may disprove previously reported works.

**Non-catalytic Ozonation of Ammonia Nitrogen**

The first paper on the non-catalytic ozonation of ammonia nitrogen was reported by Singer and Zilli [5]. The report shows that ammonia nitrogen was oxidized into nitrate under mild-alkaline conditions according to the following equilibrium:

\[
\text{NH}_3 + 4\text{O}_3 \rightarrow \text{NO}_3^- + 4\text{O}_2 + \text{H}_2\text{O} + \text{H}^+ \tag{1}
\]

The reaction was pH-dependence, that the reaction rate increases with the increase in pH of the reaction solution. In fact, the first-order rate constant for the consumption of ammonia nitrogen at mild-alkaline condition (pH 9) was about 1.5 times larger than that at pH 7, being 4.8×10^{-2} and 2.8×10^{-2} min^{-1}, respectively [5]. It was obvious that the alkalinity had an impact on the reaction rate, where the reaction between ozone and \(\text{OH}^-\) might take place to precede the oxidation of ammonia nitrogen under such conditions [6], but no information on the reaction mechanism related to the reaction of Equation 1 was given at that time.

Afterward, Hoigne and Bader [7] revealed the reason why the non-catalytic ozonation of ammonia nitrogen in [5] was pH-dependent. Eventually, they found that this was due to the change in the reaction mechanism depending on pH, being that the direct oxidation with \(\text{O}_3\) was predominant at pH < 9, while involvement of free radicals including \(\text{OH}^+\) at pH > 9. It should be noted that \(\text{OH}^+\) readily forms under alkaline conditions as the result of the decomposition of ozone by the reaction with \(\text{OH}^-\) [7]. This indicated that the reaction of Equation 1, which directly oxidizes ammonia nitrogen, governed the oxidation process only when the pH of the reaction solution was in the range from 7 to 9. Under the conditions with pH more than 9, on the other hand, the reaction between ammonia nitrogen, mainly NH₃, with free radicals predominated. From the standpoint of wastewater treatment, since ammonia nitrogen cannot be oxidized by either ozone or free radicals under acidic conditions (pH < 7), strict control of buffer materials is indispensable to maintain the alkalinity of wastewater in appropriate level during the treatment to compensate the generated proton by the reaction of Equation 1. Apparently, these two papers [5,7] are the only reports focusing on the reaction mechanism of the ozonation of ammonia nitrogen in the absence of any catalyst. Although some other reports with the same topic were published, most of the results showed the same behavior like that in references [5,7], i.e., the oxidation of ammonia nitrogen proceeds only under alkaline conditions (Table 1). Thus, it is plausible that the reaction mechanism follows either direct oxidation with ozone or free-radical pathway whenever the reaction is conducted under alkaline conditions in Figure 1 (Non-catalytic).

**Homogeneous Catalysis for Ozonation of Ammonia Nitrogen**

Br⁻ as a homogeneous catalyst

Homogeneous catalysis for the ozonation of ammonia nitrogen was firstly reported by Haag et al. [14]. The reaction was carried out under pH ranging from 7.1 to 8.4. It was reported that the presence of Br⁻ in the reaction solution significantly enhanced the oxidation rate of ammonia nitrogen with ozone. In contrast to the non-catalytic reaction where the rate was pH-dependent [5,7], the bromide-catalyzed reaction was little affected by the pH of the reaction solution. For instance, in the reaction with the initial
Krisbiantoro et al., 2020

concentrations of ammonia nitrogen and bromide were 200 and 20 µM, respectively, the first-order rate constant in ammonia nitrogen at pH 8.4 was the same as that at pH 8.1 \((k = 0.30 \text{ mg L}^{-1}\text{min}^{-1})\) and the rate was slightly decreased \((k = 0.21 \text{ mg L}^{-1}\text{min}^{-1})\) at pH 7.1. Furthermore, since the decomposition rate of ammonia nitrogen was correlated linearly with the concentration of bromine and the generation of NH₃Br was suggested in the reaction solution, it was proposed that Br⁻ in the reaction solution was firstly oxidized with ozone to form OBr⁻ at very rapid rate \((k = 160 \text{ M}^{-1}\text{s}^{-1})\) which further oxidized ammonia nitrogen into NH₃Br. Finally, NH₃Br was reacted with molecular ozone to form NO₃⁻ and Br⁻ (Figure 2, Equations 2-5). It is noted that the total reactions of Equation 2 to 5 were the same as those reported by

**Table 1.** Published papers on the non-catalytic ozonation of ammonia nitrogen.

<table>
<thead>
<tr>
<th>Reference number</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>[8]</td>
<td>Combination of ozonation with ion-exchange effectively removes ammonia nitrogen at pH higher than 8</td>
</tr>
<tr>
<td>[9,10]</td>
<td>Decomposition rate of ammonia nitrogen by ozone increases with the increase in pH and temperature</td>
</tr>
<tr>
<td>[11]</td>
<td>Under alkaline conditions the oxidation of ammonia nitrogen is governed by direct oxidation with ozone. The kinetics is first order with respect ozone and ammonia nitrogen</td>
</tr>
<tr>
<td>[12]</td>
<td>At pH ranging from 6.5 to 9.0, the effect of Cl⁻ is negligible on the oxidation of ammonia nitrogen in seawater with ozone</td>
</tr>
<tr>
<td>[13]</td>
<td>Ozone microbubbles is effective for ozonation of ammonia nitrogen at high pH and high ozone generation rate</td>
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</table>

**Figure 1.** Summary for the reaction pathways of the oxidation of ammonia nitrogen with ozone in the absence and presence of catalyst summarizes from [5,7,14,15] as well as the unpublished works by the first and second authors.
Singer and Zilli, in which 4 ozone molecules are needed to oxidize one ammonia nitrogen (Equation 1).

\[
\text{O}_3 + \text{Br}^- \rightarrow \text{OBr}^- + \text{O}_2 \quad (2)
\]

\[
\text{H}^+ + \text{OBr}^- \rightarrow \text{HOBr} \quad (3)
\]

\[
\text{HOBr} + \text{NH}_3 \rightarrow \text{NH}_2\text{Br} + \text{H}_2\text{O} \quad (4)
\]

\[
3\text{O}_3 + \text{NH}_2\text{Br} \rightarrow 2\text{H}^+ + \text{NO}_3^- + \text{Br}^- + 3\text{O}_2 \quad (5)
\]

**Figure 2.** The reactions involving Br⁻ for the ozonation of ammonia nitrogen (the figure was obtained by the modification of that in [16] and the rate constant was obtained from [14]).

Haag et al. suggested that NH₂Br was the intermediate formed during the ozonation reactions (noted that NH₂Br is predominant bromamine species at mild-alkaline condition [17]). However, the concentration of NH₂Br was determined in an indirect manner, i.e., from the pH and the total ammonia nitrogen and bromine derived from equilibrium constant given in reference [17]. Therefore, it is unlikely that NH₂Br is the only intermediate, but it is possible that NHBr₂ or NB₃ might be involved in the reaction mechanism. Nevertheless, this paper made significant progress in terms of ammonia nitrogen removal from wastewater because the independency to pH of the reaction solution makes this method is readily applicable for wastewater treatment without the necessity of pH adjustment.

**Cl⁻ as a homogeneous catalyst**

Recently, Liu et al. proposed the reaction mechanism for the ozonation of ammonia nitrogen in the presence of Cl⁻ at 283 K and under wide pH range from acidic to mild-alkaline. As being similar to [5] and [7], Liu et al. suggested that the reaction was pH-dependent. Under alkaline conditions, ammonia nitrogen was oxidized through direct oxidation with ozone as well as by free radicals, including OH⁺ as shown in Figure 1. However, at low pH, the presence of Cl⁻ in the reaction solution leads to another reaction pathway. It was proposed that Cl⁻ in the reaction solution was firstly oxidized with ozone to form ClO⁻ (Equations 6-8) which further oxidized NH₄⁺ to N₂ and NO (Equations 9-12).

\[
\text{Cl}^- + \text{O}_3 \rightarrow \text{ClO}^- + \text{O}_2 \quad (6)
\]

\[
\text{Cl}^- + \text{O}_3 \rightarrow \text{ClO}^- + \text{O}_2 \quad (7)
\]

\[
\text{ClO}^- \rightarrow \text{ClO}_2^- + \text{O}_2 \quad (8)
\]

\[
3\text{ClO}^- + 2\text{NH}_4^+ \rightarrow \text{N}_2 + 3\text{Cl}^- + 2\text{H}^+ + 3\text{H}_2\text{O} \quad (9)
\]

\[
4\text{ClO}^- + 2\text{NH}_4^+ \rightarrow \text{N}_2\text{O} + 4\text{Cl}^- + 2\text{H}^+ + 3\text{H}_2\text{O} \quad (10)
\]

\[
3\text{ClO}_2^- + 2\text{NH}_4^+ \rightarrow \text{N}_2 + \text{Cl}^- + 2\text{H}^+ + 3\text{H}_2\text{O} \quad (11)
\]

\[
4\text{ClO}_2^- + 6\text{NH}_4^+ \rightarrow 3\text{N}_2\text{O} + 4\text{Cl}^- + 6\text{H}^+ + 9\text{H}_2\text{O} \quad (12)
\]

As shown in Equations 9-12, Cl⁻ was regenerated by the reaction of NH₄⁺ with ClO⁻, meaning that Cl⁻ catalytically promoted the reaction. They suggested that the final products by the catalytic reaction were mainly N₂ and N₂O. However, this result was quite different to that reported in [5], where it was reported that the reaction in the presence of Cl⁻ under mild-alkaline conditions gave results analogous to that in the absence of Cl⁻. The report showed that Cl⁻ was insignificant to the oxidation rate of ammonia nitrogen and NO⁻ was generated as the main product [5]. This difference suggested that the presence of Cl⁻ had a significant impact on the reaction pathway as well as the products when the pH of the reaction solution was acidic, meaning that NH₄⁺ existed predominantly. Meanwhile, under alkaline conditions, the involvement of Cl⁻ was much less significant and Cl⁻ did not impact the reaction of NH₄ with O₃ or free radicals [15]. Therefore, the pH of the reaction solution did not only affect the reaction pathway of the ozonation of ammonia nitrogen with ozone in the presence of Cl⁻ but also the products.

Recently, the research group of the authors revealed that the concentration of Cl⁻ in the reaction solution was decreased along with the decrease of the concentration of NH₄⁺ for the ozonation of ammonia nitrogen in the presence of Cl⁻ (Figure 3) [18]. The behavior of Cl⁻ in the reaction solution was in contrast to the reaction pathway proposed by Liu et al. shown in Equations 5-8, because Cl⁻ was consumed with reaction time. In addition, instead of gaseous nitrogen compounds, we observed that nitrate was formed as the main product with 55% selectivity. Meanwhile, no reaction occurred when (NH₄)₂SO₄ was used as a reactant to prepare the reaction solution instead of NH₄Cl. Furthermore, it was revealed that the formation of chloramines (NH₃·xCl⁻, x = 1-3) was the reason for the decrease of Cl⁻.
Therefore, we concluded that the oxidation of ammonia nitrogen with ozone in the presence of Cl⁻ formed chloramines in addition to NO₃⁻ and other gaseous nitrogen compounds, which were presumably N₂ and N₂O (Homogeneous catalysis with Cl⁻ in Figure 1) [18].

Ozonation of ammonia nitrogen catalyzed with Pd²⁺ in the presence of Cl⁻: a preliminary report

In this section, the authors would like to report that Pd²⁺ was a highly active homogeneous catalyst for ozonation of ammonia nitrogen in the presence of Cl⁻ under mild-acidic conditions. Figure 4(a) shows the conversion of ammonia nitrogen over Pd²⁺ in the reaction solutions prepared with (NH₄)₂SO₄ and NH₄Cl, which denoted as Sol-SO₄ and Sol-Cl, respectively. As a comparison, the data for the blank experiment is shown in the figure. No reaction occurred in Sol-SO₄ regardless of the absence and presence of Pd²⁺. In contrast, the addition of Pd²⁺ significantly increased the conversion for the reaction in Sol-Cl. While the conversion was 13% in the absence of Pd²⁺ (blank Sol-Cl) at 6 h, the near-complete conversion was obtained in the presence of Pd²⁺.

To get insight on the reaction pathway, the behavior of ionic species in the reaction solution was monitored by using ion chromatography. Figure 4(b) shows the relative concentration of NH₄⁺ and Cl⁻ as well as the selectivity to gaseous nitrogen compounds for the reaction with Pd²⁺ in Sol-Cl. In contrast to the homogeneous catalysis by Cl⁻ (Figure 3), the decomposition rate of NH₄⁺ in Sol-Cl in the presence of Pd²⁺ was very fast, being 3.5 mmol h⁻¹.

Figure 3. Ozonation of ammonia nitrogen in the presence of Cl⁻. Reaction conditions: 10 mmol L⁻¹ NH₄Cl solution, 100 mL; initial pH, 7.0; total flow rate of O₃/O₂ mixture, 100 mL min⁻¹; concentration of O₃ in the mixture, 0.7 vol%; and reaction temperature, 333 K. (●) NH₄⁺, (○) Cl⁻.

Figure 4. Ozonation of ammonia nitrogen in Sol-SO₄ and Sol-Cl (prepared from (NH₄)₂SO₄ and NH₄Cl, respectively) in the absence and presence of Pd²⁺ (a) and the behavior of NH₄⁺ and Cl⁻ as well as the selectivity to gaseous nitrogen compounds for the reaction in Sol-Cl in presence of Pd²⁺ (b). Reaction conditions: catalyst, 10 mmol L⁻¹ Pd(NO₃)₂ solution; 10 mmol L⁻¹ NH₄⁺ solution, 100 mL; initial pH, 7.0; total flow rate of O₃/O₂ mixture, 100 mL min⁻¹; concentration of O₃ in the mixture, 0.7 vol%; reaction temperature, 333 K; and reaction time, 6 h. (●) NH₄⁺, (○) Cl⁻.
decomposition of ammonia nitrogen with ozone in Fe heterogeneous catalysis was first reported by Ichikawa et al. [1]. Nevertheless, not much progress has been made in the ozonation of ammonia nitrogen. Therefore, catalytic ozonation is quite important in this topic. Kasprzyk et al. [2] summarized the reports on catalytic ozonation of ammonia nitrogen over metal oxides in the presence of Cl\(^{-}\). Reaction conditions: 10 mmol L\(^{-1}\) NH\(_3\)Cl solution, 100 mL; initial pH, 7.0; total flow rate of O\(_3\)/O\(_2\) mixture, 100 mL min\(^{-1}\); concentration of O\(_3\) in the mixture, 0.7 vol\%; reaction temperature, 333 K; and reaction time, 6 h (adapted from [2]).

About 98% conversion was achieved only at 3 h with the selectivity to gaseous nitrogen of ca. 80%, which was independent over the reaction time. However, being similar to the reaction in the absence of Pd\(^{2+}\) shown in Figure 4, Cl\(^{-}\) was consumed in the reaction solution. Although the investigation for the role of Cl\(^{-}\) in this reaction is still under investigation, it is likely that the reaction follows ClO\(_{3}^{-}\) pathway (Homogeneous catalysis in Figure 1). Moreover, because Pd\(^{2+}\) and Cl\(^{-}\) readily form complex in water, the formation of Pd–Cl or Pd–ClO\(_{3}^{-}\) complex may be involved in the reaction mechanism.

**Heterogeneous catalysis for ozonation of ammonia nitrogen**

For the last two decades, the studies on the catalytic ozonation over heterogeneous catalysis have been intensively studied, and the reports on this topic were well summarized by Nawrocki and Kasprzyk-Hordern [19]. While the progress in heterogeneous catalytic ozonation is quite steady for degradation of organic pollutants, that in the catalytic ozonation of ammonia nitrogen seems to be little. Nevertheless, not much progress also can be caused by the fact that the first report was published just 6 years ago by Ichikawa et al. [2].

**Heterogeneous catalysis over Co\(_{3}O_{4}\)**

Ichikawa et al. reported that metal oxides, including MgO, NiO, Co\(_{3}O_{4}\), CuO, ZnO, MnO\(_{2}\), FeO\(_{3}\), SnO\(_{2}\), and Al\(_{2}O_{3}\) showed activity for the decomposition of ammonia nitrogen with ozone in the presence of Cl\(^{-}\) under mild-acidic conditions at 333 K (Figure 5). While MgO was the best catalyst in terms of activity but the lowest selectivity to gaseous nitrogen compounds, Co\(_{3}O_{4}\) showed the highest selectivity with moderate activity.

Because Co\(_{3}O_{4}\) was the most potentially applicable for practical use due to high selectivity to gaseous nitrogen compounds, the mechanistic study was focused on the reaction over Co\(_{3}O_{4}\). It was reported that under the reaction conditions, Cl\(^{-}\) was indispensable to proceed the oxidation reaction with ozone. Thus, it was proposed that Cl\(^{-}\) was firstly oxidized by O\(_{3}\) over Co\(_{3}O_{4}\) to form ClO\(_{3}^{-}\), which further oxidized NH\(_{3}\) [2]. However, there were several things that needed further clarification in this paper:

- The dissolution degree of NiO (56%) and MgO (38%) were simply too high. It is unlikely that the dissolution was solely caused by the hydrolysis of the materials.
- No information on Cl\(^{-}\) balance during the reaction was available; it is possible that chloramines (NH\(_{3}\)-Cl) might be formed by the reaction of ClO\(_{3}^{-}\) with ammonia nitrogen.

Mahardiani and Kamiya [20] reported that the catalytic activity of Co\(_{3}O_{4}\) for the ozonation of ammonia nitrogen in the presence of Cl\(^{-}\) was greatly enhanced with each reuse under the reaction conditions similar to those in [2]. It was proposed that the formation of –NH\(_{2}\) group on Co\(_{3}O_{4}\) was the reason for the enhancement. Although the effect of calcination temperature of Co\(_{3}O_{4}\) on the enhancement
indicated that the enhancement appeared only when CoO was calcined at a lower temperature, i.e., surface hydroxyl group was involved in the enhancement; however, there was no direct evidence for the formation of –NH₃⁺ on the surface. Thus, the reliable mechanism behind this enhancement is still unknown. Nevertheless, since the intensity of the diffraction line at 2θ = 36°, which correspond to (311) plane, was decreased after the enhancement appeared (Figure 6), it is likely that the enhancement in catalytic activity might be caused by the change in the particle size of CoO. For instance, the smaller particle size might also cause an increase in catalytic activity.

![Figure 6. Powder XRD patterns of (a) fresh CoO and (b) CoO after reused for nine times (adapted from [20]).](image)

Afterward, Mahardiani investigated the catalytic activity of CoO spinal, CoO wurtzite and CoO(OH) for the ozonation of ammonia nitrogen in the presence of Cl⁻ [21]. Eventually, it was revealed that the activity over CoO was much higher than those in the presence of CoO and CoO(OH) but the selectivity to gaseous nitrogen compounds over CoO(OH) was higher than that over CoO. The reason for the high activity of CoO was proposed as CoO possessed more dispersed Co²⁺ species on the surface compared to CoO and CoO(OH). Meanwhile, the high selectivity of CoO(OH) was suggested to be caused by the high surface density of adsorbed NH₃ compared to high O²⁻ adsorbed on the surface of CoO.

Recently, we performed a systematic investigation on the reaction mechanism in the presence of CoO for the ozonation of ammonia nitrogen in the water. As mentioned above, Ichikawa et al. reported that Cl⁻ was indispensable for the reaction and that N₂ and N₂O were the main products [2]. However, in our recent work [22], it was found that Cl⁻ was consumed for the reaction and the formation of trichloramine was the reason for this consumption. Nevertheless, the reaction mechanism over CoO was basically the same as that reported by Ichikawa et al., i.e., followed ClO⁻ pathway.

**Heterogeneous catalysis over MgO**

Chen et al. reported that a composite containing CoO and MgO (Mg:Co = 4:1) was a more active catalyst than pristine CoO under mild-alkaline conditions and worked even at room temperature as reported in [23]. It was proposed that under alkaline conditions, ozone first gave OH⁻ by the reaction with OH⁻ (Equations 9-11) which further oxidized NH₃ into N₂ and NO₃⁻ (Equations 12-15).

\[
\begin{align*}
O_3 + OH & \rightarrow HO_2\cdot + O_2\cdot + \text{(aq)} \\
O_3 + HO_2\cdot & \rightarrow OH\cdot + 2O_2 \\
4NH_3 + O_3 & \rightarrow 2N_2 + 3H_2O + 6H^+ \\
2NH_3 + OH\cdot & \rightarrow N_2 + H_2O + 5H^+ \\
NH_3 + 6OH\cdot & \rightarrow NO_3^- + 4H_2O + H^+ \\
NO_3^- + 2OH\cdot & \rightarrow NO_3^- + H_2O \\
NH_3 + 8OH\cdot & \rightarrow NO_3^- + 5H_2O + H^+ 
\end{align*}
\]

The problem with this research is that the leaching behavior of MgO was not deeply considered and there was no information on how pH of the reaction solution was maintained around mild-alkaline while protons were generated by the reactions (Equations 11-13, 15).

Afterward, Liu et al. reported that MgO prepared by precipitation method acted as solid alkali as well as catalyst for the oxidation of ammonia nitrogen at 283 K under alkaline conditions [15]. Two mechanisms were proposed: 1) ammonia nitrogen was directly oxidized with ozone on the hydroxylated surface of MgO and 2) both ammonia nitrogen and ozone were adsorbed and subsequently reacted on the surface of MgO (Figure 7). Similar to Chen et al. [23] it was not mentioned the dissolution behavior of MgO into the reaction solution during the reaction.

In contrast to previous papers on the use of MgO catalyst, we found that MgO was actually acted as a reactant instead of catalyst (Equation 16) and the reaction mechanism in the presence of MgO was revealed to follow a radical pathway [22].
NH₃ + O₃ → NO₃⁻ + 4O₂ + Mg²⁺ + 2H₂O  (16)

**Figure 7.** Proposed mechanism for ozonation of ammonia nitrogen over MgO by Liu et al. [15].

**Heterogeneous catalysis over Pd/CeO₂**

In the middle of 2019, the first author found that Pd/CeO₂ was a very active catalyst, being able to completely remove ammonia nitrogen within 3 h (Figure 8) with 90% selectivity to gaseous nitrogen compounds. Since we will submit this report for publication, in this short review, we provide only conclusions of the study. We found that the reaction pathway over Pd/CeO₂ followed ClO⁻ pathway with chlorammines formation as the main product (Figure 1).

**Figure 8.** Time-course changes in the concentrations of (●) NH₄⁺, (△) Cl⁻ and (□) NO₃⁻ for the ozonation of NH₄⁺ in Sol(Cl) over Pd/CeO₂. Reaction conditions: catalyst weight, 0.1 g; loading amount of Pd, 5wt.%; 10 mmol L⁻¹ NH₄Cl solution, 100 mL; initial pH, 7.0; total flow rate of O₃/O₂ mixture, 100 mL min⁻¹; concentration of O₃ in the mixture, 0.7 vol%; and reaction temperature, 333 K.

**Conclusions**

It is obvious that ozonation is a very efficient method for the removal of ammonia nitrogen in wastewater because the reaction can proceed at low temperature and atmospheric pressure. Despite the fact that some reports have been published, the understanding of the reaction mechanism, especially for the reaction in the presence of the catalyst, is still poor. For homogeneous catalysis, so far, only three catalysts, including Cl⁻, Br⁻ and Pd²⁺ (in the presence of Cl⁻) were found to be active for the reaction. Meanwhile, for heterogeneous catalysis, only two materials e.g., CoO₃ and MgO had been reported until the first author found that Pd/CeO₂ was extremely active for the reaction. Following points are what we know in regard to the reaction mechanisms for the oxidation reaction of ammonia nitrogen with ozone:

- Ammonia nitrogen can be directly oxidized with ozone under mild-alkaline condition and oxidized with free radicals (including OH•) at high pH.
- While homogeneous catalytic ozonation with Br⁻ can works at neutral to mild-alkaline pH, the Cl⁻ catalyzed reaction only can proceed under acidic condition.
- Heterogeneous catalysis with CoO₃ and Pd/CeO₂ followed ClO⁻ pathway.

Finally, it is concluded that very few reports might be caused by the fact that not so many routes can be taken to oxidize ammonia nitrogen in the water. Nevertheless, the window in heterogeneous catalysis is still wide open, especially for the oxidation reaction that can proceed even in the absence of Cl⁻ or Br⁻.

**Conflict of Interest**

There is no conflict of interest to declare.

**References**


